EMSP COLLABORATIONS

Research results are not always directly transferred to a specific end-user. Collaborations or interactions between EMSP researchers and others occur that increase the body of knowledge in a specific area as a direct result of EMSP funded research. This comes in many forms:

- 40 Consulting - provide advice or technical expertise
- 8 Joint interaction - researcher and end-user in joint interaction
- 13 Mission directed - project direction provided by end-user
- 26 Program interaction - researcher to researcher interaction
- 1 Unclassified.

This section describes the reported collaborations that have occurred within the EMSP. Numerous other less formal collaborations occur during the EMSP topical and national workshops. Many of these are anticipated to mature into the research partnerships and research transfers reported elsewhere in this document.

Project: 54506

Title: Acid-Base Behavior in Hydrothermal Processing of Wastes
PI: Dr. Keith P. Johnston *Institution:* University of Texas at Austin

Description: A new technology, hydrothermal oxidation (also called supercritical water oxidation), is being developed to treat high level nuclear wastes. Nitrates are reduced tonitrogen; furthermore, phosphates, alumina sludge, and chromium are solubilized, and the sludge is reconstituted as fine oxide particles. A major obstacle to development of this technology has been a lack of scientific knowledge of chemistry in hydrothermal solution above 350 C, particularly acid-base behavior, and transport phenomena, which is needed to understand corrosion, metal-ion complexation, and salt precipitation and recovery. In an effort to understand these problem, collaborative work with LANL on experimentally treating tank waste with high temperatures is underway.
Collaboration Type: Joint interaction *Collaborator:* Steve Buelow
Collaborating Organization: LANL

Project: 54546

Title: Engineered Antibodies for Monitoring of Polynuclear Aromatic Hydrocarbons
PI: Dr. Alexander E. Karu *Institution:* UC Berkeley

Description: The objective of this project is to use molecular biological techniques to derive a set of antibodies with useful affinities and selectivities for recovery and detection of polynuclear aromatic hydrocarbons (PAHs) in environmental and biological samples. The long-term goal is to develop immunodetection methods that will be useful in biomarker research and regulatory monitoring of PAHs. This project has established a collaboration with Dr. Tuan Vo-Dinh at ORNL to identify a sensor system and perform a demonstration.

Collaboration Type: Mission directed *Collaborator:* Dr. Tuan Vo-Dinh

Collaborating Organization: ORNL

Project: 54656

Title: Mixing Processes in High-Level Waste Tanks

PI: Dr. Per F. Peterson *Institution:* UC Berkeley

Description: Flammable gases can be generated in DOE high-level waste tanks. This project is a concentrated effort to develop models and a numerical tool to mechanistically predict mixing processes in large waste-tank volumes, where mixing processes can be driven by hot and cold vertical and horizontal surfaces and injected buoyant jets. General Electric is funding a doctoral student to work on this project.

Collaboration Type: Consulting

Collaborating Organization: General Electric

Project: 54672

Title: Radiation Effects in Nuclear Waste Materials

PI: Dr. William J. Weber *Institution:* Pacific Northwest National Laboratory

Description: The PI was requested to assist in evaluating potential radiation-induced failure of protective glass globes for lights in the in-tank camera systems for Tank 101-SY at Hanford. Unexplained failure of two globes had raised some safety concerns. Working with Lockheed Martin Hanford Co. staff, an interim testing program was designed for the protective glass globes, a procedure to minimize potential failure (change globes frequently) was advised, and some preliminary measurements and evaluations were conducted on irradiated globes. No permanent solution was developed as yet.

Collaboration Type: Consulting *Collaborator:* Scott M Werry

Collaborating Organization: Lockheed Martin Hanford Co.

Description: The effects of radiation from the decay of radionuclides in nuclear waste and other nuclear materials may potentially impact the long-term performance and stability of nuclear waste forms and stabilized nuclear materials. Using experimental and computer simulation approaches, this project endeavors to develop the underpinning science and models necessary to assess the effects of radiation on the performance of glasses and ceramics designed for the immobilization of high-level tank waste and stabilized nuclear materials. Collaborations with PNNL and LANL have been developed to help further these objectives.

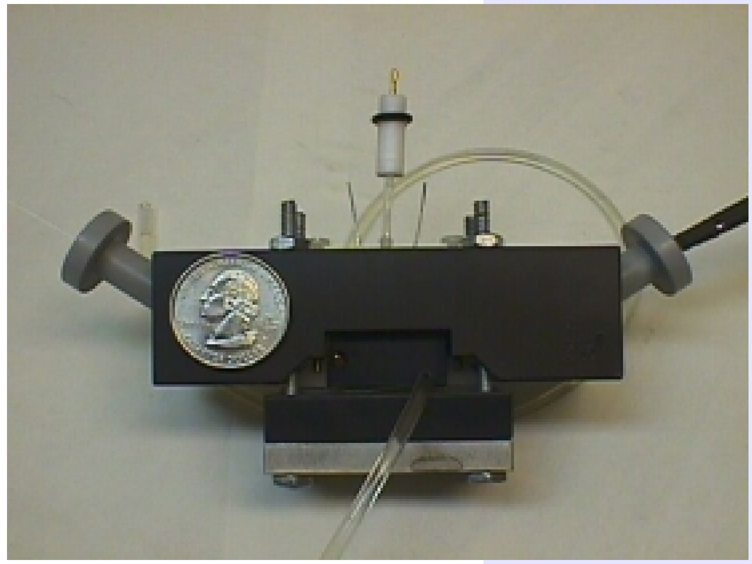
Collaboration Type: Program interaction *Collaborator:* N.J. Hess, B.D. Begg, L.R. Corrales, H.L. Heinisch, and R.E. Williford; S.D. Conradson

Collaborating Organization: PNNL, LANL

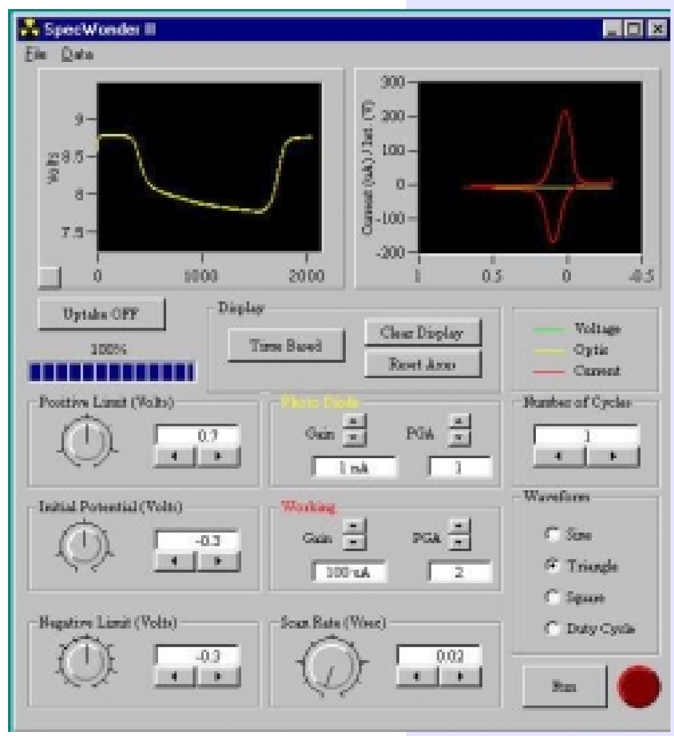
Project: 54674

Title: Design and Development of a New Hybrid Spectroelectrochemical Sensor
PI: Dr. William R. Heineman
Institution: University of Cincinnati

Description: A proposed new sensor concept proposed combines the elements of electrochemistry, spectroscopy and selective partitioning into a single device that provides three levels of selectivity. This type of sensor has many potential applications at DOE sites. As an example, the enhanced specificity embodied in this new sensor design is well-suited to the analytical problem posed by the addition of ferrocyanide to radioactive tank wastes at the USDOE Hanford Site. A demonstration of a sensor package (mircocell and Instrumentation) was performed on waste tank sample.
Collaboration Type: Program interaction
Collaborator: Dr. Heineman - University of Cincinnati
Collaborating Organization: Hanford Site



Prototype sensor can accommodate a sample volume of 800 mL. Working electrode consists of an indium tin oxide slide coated with a charge selective film; the blue LED provides a simple light source. [see Project #54674]



Virtual Software interface for spectroelectrochemical sensor provides remote control of sensor and remote monitoring of sensor response. [see Project #54674]

Project: 54679

Title: Architectural Design Criteria for F-Block Metal Ion Sequestering Agents
PI: Dr. Benjamin P. Hay
Institution: Pacific Northwest National Laboratory

Description: Critical tasks in the cleanup of U.S. Department of Energy (DOE) sites include processing radioactive wastes for disposal in long-term storage, remediation/restoration of environmental sites resulting from radioactive contamination, and decontamination/decommissioning of nuclear facilities. Because the radioactive components, most of which are metals, are typically present in very low concentrations, it is desirable to remove them from the bulk of the contaminated source and concentrate them to minimize the volume of radioactive material destined for permanent subsurface disposal and thus minimize disposal costs. Over the past 50 years, much research has focused on the discovery of selective ligands for f-block metal separations; both neutral and ionic ligands have been examined. Despite past success in the discovery of ligands that exhibit some degree of specificity for the f-block metal ions, the ability to further control binding affinity and selectivity remains a significant challenge. The objective of this project is to provide the means to optimize ligand architecture for f-block metal recognition. Criteria for accurately selecting target ligands would result in a much more effective use of resources, thereby reducing the time and cost associated with metal-specific ligand development. Collaborations for each associated task are as follows: Task: Synthesis and characterization of modified calixarene host molecules. Professor D. Max Roundhill, Department of Chemistry, Texas Tech UniversityTask: Crystal structure determinations. Professor Robin D. Rogers, Department of Chemistry, The University of AlabamaTask: Synthesis of amides and diamides, through a subcontract with Associated Western Universities to support a Postdoctoral Fellow, Dr. Robert Gilbertson, In Dr. Hutchison's group. Professor James E. Hutchison, Department of Chemistry, University of OregonTask: Provide structure-function data on catecholates and hydroxypyridonates. Professor Kenneth N. Raymond, Department of Chemistry, University of California at BerkeleyTask: Provide structure-function data on pyridine N-oxides. Professor Robert T. Paine, Department of Chemistry, University of New MexicoIn addition to interactions with University faculty, the project has supported a variety of visitors at Pacific Northwest National Laboratory through Associated Western Universities subcontracts, including: Dr. Pier L. Zanonato (Visiting Faculty, University of Padova, Italy) - calorimetry Dr. Bruce K. McNamara (Postdoctoral Fellow) - calorimetry, spectroscopy, solventextraction. Dr. Omoshile Clement (Postdoctoral Fellow) - molecular mechanics Dr. Giovanni Sandrone (Postdoctoral Fellow) - quantum mechanics. Dr. Rubicelia Vargas (Post Doctoral Fellow) - molecular mechanics and quantummechanics Dr. Jorge Garza (Visiting Faculty, Metropolitan Autonomous University - Iztapalapa, Mexico) - quantum mechanics.

Collaboration Type: Program interaction *Collaborator:* (see description)
Collaborating Organization: (see description)

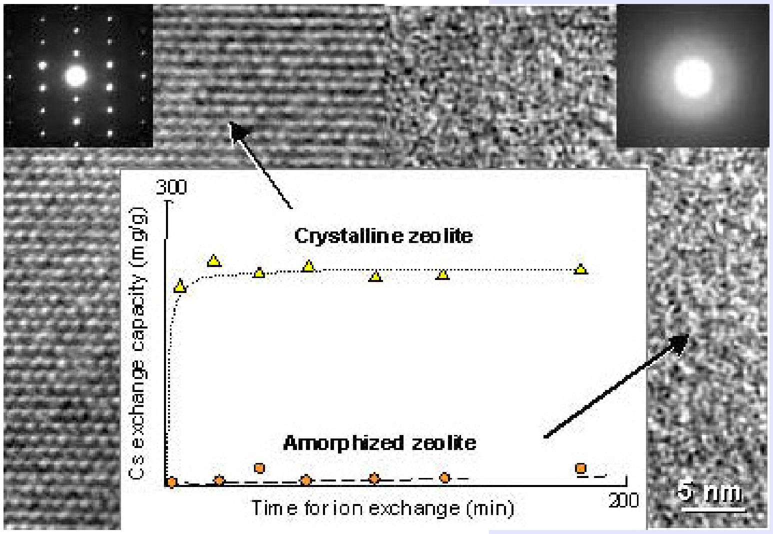
Project: 54684

Title: Mechanism Involved in Trichloroethylene-Induced Liver Cancer: Importance to Environmental Cleanup

PI: Dr. Richard J. Bull *Institution:* Pacific Northwest National Laboratory

Description: EPA is using the data we have generated and a paper describing the mode of action for induction of liver tumors to revise their risk assessment on trichloroethylene. EPA continues to track our published results as this decision process reaches its conclusions. A separate step will be actions taken under the Office of Water to revise drinking water standards or CERCLA to modify clean-up standards that are derived from the revised risk assessments.

Collaboration Type: Consulting
Collaborating Organization: EPA



Effect of solid-state amorphization on Cs exchange capacity of zeolite. As demonstrated by University of Michigan, zeolite lost 95% of its Cs exchange capacity after solid-state amorphization. [see Project #54691]

Project: 54691

Title: Radiation Effects on Materials in the Near-Field of Nuclear Waste Repository
PI: Dr. Lu-Min Wang
Institution: University of Michigan

Description: The objective of this research program has been to evaluate the long-term radiation effects in materials used in processing high-level nuclear waste or materials in the near-field of a nuclear waste repository. This program has established the following collaborations: Dr M. L. Balmer (PNNL), and Dr. T. M. Nenoff (SNL) - EMSP Project 60345. We have studied radiation effects on samples associated with the development of new silicotitanate waste form development provided by their research groups and provided data to them. Dr. G. Liu (ANL) - EMSP Project 55367. Information and experience exchanged on radiation damage studies. Prof. A. Clearfield (Texas A&A University) - EMSP Project 54735. We have obtained silicotitanate samples synthesized by Prof. Clearfield and conducted a preliminary study on radiation effects in the sample. Dr. W.J. Weber (PNNL) - EMSP Project 54672. Information and experience exchange on radiation damage studies.

Collaboration Type: Consulting
Collaborator: (see descriptions)
Collaborating Organization: (see descriptions)

Two commercial partners have applied for a license for the High Fluence Neutron Source, shown here in the laboratory. [see Project #54751]

Project: 54741

Title: Characterization of Contaminant Transport Using Naturally-Occurring U-Series Disequilibria
PI: Dr. Michael T. Murrell

Institution: Los Alamos National Laboratory

Description: Consulted regarding uranium measurements at Rocky Flats by contractors for Rocky Flats and for the State of Colorado. We later received a small amount of funding to make some measurements for solar pond waters at Rocky Flats. The approach used was similar to that of our EMSP project.
Collaboration Type: Consulting
Collaborator: : Dave Janecky
Collaborating Organization: Rocky Flats Environmental Technology Site, State of Colorado

Project: 54751

Title: High Fluence Neutron Source for Nondestructive Characterization of Nuclear Waste
PI: Dr. Mark M. Pickrell
Institution: Los Alamos National Laboratory

Description: The objective of the project is to research the basic plasma physics necessary to develop a high fluence neutron source based on the inertial electrostatically confined (IEC) plasma. An intense neutron source directly addresses the capability to characterize nuclear materials under difficult measurement conditions. Some of the applications for Environmental Management are the characterization of TRU wastes for WIPP, the measurements of residues prior to stabilization and disposal, the measurements of cemented or vitrified wastes, the measurement of spent nuclear fuel, and the measurement of high level wastes. Collaborations with the INEEL and the National Spent Nuclear Fuels Program to produce a neutron source for MDAS or other systems being developed by the INEEL.
Collaboration Type: Mission directed *Collaborator:* Jerry Cole
Collaborating Organization: Idaho National Engineering and Environmental Laboratory

Project: 54828

Title: Processing of High Level Waste: Spectroscopic Characterization of Redox Reactions in Supercritical Water
PI: Dr. Charles A. Arrington, Jr. *Institution:* Furman University

Description: Collaborative research effort with LANL on the destructions of complexants and oxidation of chromium and technetium by hydrothermal processing in near critical or supercritical aqueous solutions.
Collaboration Type: Mission directed *Collaborator:* Steven Buelow and Jeanne Robinson
Collaborating Organization: LANL

Project: 54926

Title: Novel Ceramic-Polymer Composite Membranes for the Separation of Hazardous Liquid Waste
PI: Dr. Yoram Cohen *Institution:* UCLA

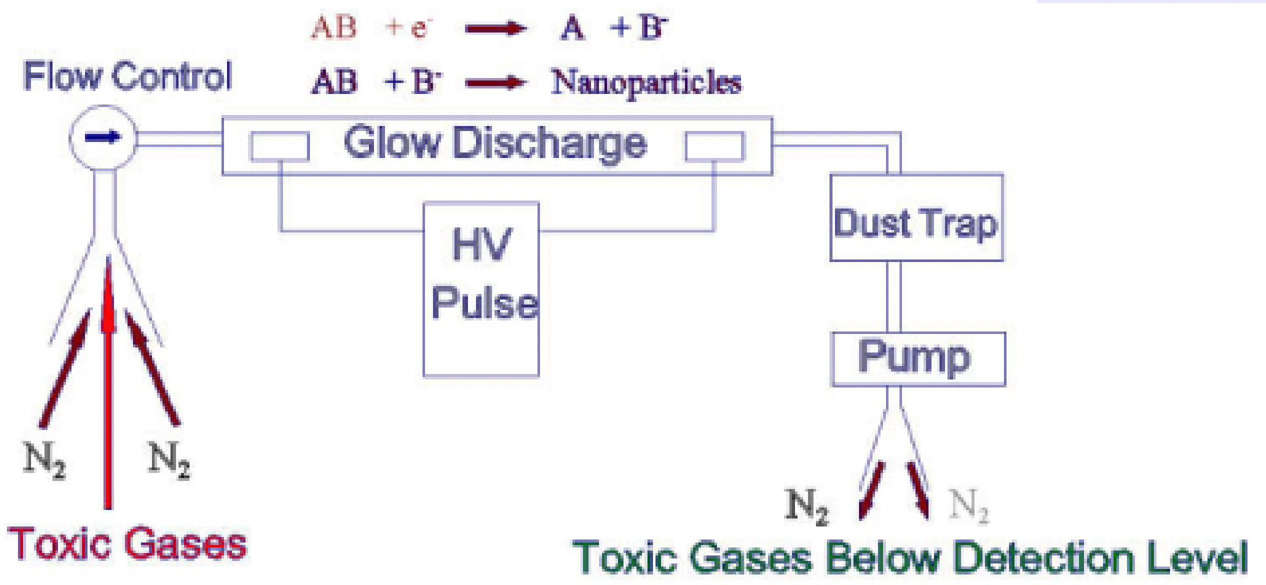
Description: There is a growing need in the areas of hazardous waste treatment, remediation and pollution prevention for new processes capable of selectively separating and removing target organic species from aqueous steams. Membrane separation processes are especially suited for solute removal from dilute solutions. They have the additional advantage of requiring less energy relative to conventional separation technologies (e.g., distillation, extraction and even adsorption processes). The major difficulty with current membranes is the poor longevity of polymeric membranes under harsh conditions (high temperature, harsh solvents and pH conditions) and the lack of selectivity of ceramic membranes. In our previous work (1996 EMSP project), a first generation of novel polymer-ceramic (PolyCer) composite membranes were developed with the goal of overcoming the above difficulties. The proposed PolyCer membranes are fabricated by a surface-graft polymerization process resulting in a molecular layer of polymer chains which are terminally and covalently anchored to the porous membrane support. We have worked with scientists at the DOE/EMSL facility to characterize the surfaces of our membranes by Atomic Fore Microscopy (AFM) and also by SEM and XPS. We submitted a proposal to EMSL which was accepted. Subsequently the PI (Dr. Y. Cohen) spent about 4 days at the EMSL facility and his doctoral student (Wayne Yoshida) visited the EMSL facility for a period of three weeks.

Collaboration Type: Program interaction
Collaborating Organization: EMSL

Project: 54973

Title: A Novel Energy-Efficient Plasma Chemical Process for the Destruction of Volatile Toxic

PI: Dr. Lal A. Pinnaduwage *Institution:* Oak Ridge National Laboratory



Remediation of Toxic Gas Streams. [see Project #54973]

Description: Removal of low-concentrations (below several percent) of volatile toxic compounds (VTCs) from contaminated air streams is encountered at DOE waste sites in two instances*:* (i) Off-gases resulting from air-stripping of contaminated soil and water. (ii) Effluent from the incineration of highly-concentrated combustible hazardous wastes. The objective of our research program is to develop a novel plasma chemical process for the destruction of VTC's in low- concentration waste streams. Discussion have been initiated to determine applicability of this work to Paducah groundwater treatment problems and assess site interest. Mr. Richards expressed considerable interest in this approach and noted the timeframe of availability (assuming follow-on funding for development) was compatible with site plans.

Collaboration Type: Consulting *Collaborator:* Walt Richards

Collaborating Organization: Bechtel Jacobs Company, Paducah, KY

Project: 54996

Title: Ionizing Radiation Induced Catalysis on Metal Oxide Particles

PI: Dr. Michael A. Henderson *Institution:* Pacific Northwest National Laboratory

Description: This project focuses on a novel approach for destroying organics found in high-level mixed waste prevalent at DOE sites. We have shown that ionizing radiation can be used to catalytically destroy organic chelating agents, such as EDTA, whose presence in high-level waste streams hinder the removal of radionucleii by ion exchange. Our studies have shown that gamma irradiation of titanium dioxide suspensions destroy the chelating ability of EDTA by decomposing it to smaller organic molecules. This has been demonstrated for both free EDTA in solution and for solutions of EDTA complexed to strontium. Present efforts are aimed at determining the mechanism by which EDTA is destroyed and the feasibility of using this process for treating high-level mixed waste.

Collaboration Type: Consulting *Collaborator:* Abhaya K. Datye; Professor Miguel E. Castro

Collaborating Organization: University of New Mexico; University of Puerto Rico

Project: 55036

Title: Colloid Transport and Retention in Fractured Deposits

PI: Dr. John F. McCarthy *Institution:* Oak Ridge National Laboratory

Description: The goal of the project was to identify the chemical and physical factors that control the transport of colloids in water-saturated fractured formations, and develop a generalized capability to predict colloid attachment and detachment based on hydraulic factors, physical structure, and chemical properties. The research targeted multiple scales, including (a) mechanistic description and experiments colloid dynamics in fractures; (b) colloid transport experiments in undisturbed geological monoliths; (c) field-scale colloid transport experiments; and (d) modeling of colloid transport in complex fracture networks. Fundamental Description Of Particle Transport In Fracture. Dr. David Walker, Cardiff University, United Kingdom Colloid Transport In Intact Geological Column,sDr. Larry D. McKay, University of TennesseeField-Scale Colloid Tracer Migration, Dr. William E. Sanford, Colorado State University, Ms. Paige L. Stafford, University of Tennessee Fracture Network Models of Colloid Transport, Dr. Motomu Ibaraki, Ohio State University.

Collaboration Type: Program interaction *Collaborator:* (see description)
Collaborating Organization: (see description)

Project: 55094

Title: Chemical and Ceramic Methods Toward Safe Storage of Actinides Using Monazite
PI: Dr. P. E. D. Morgan *Institution:* Rockwell International Corporation

Description: The interaction between electron beams and the rare-earth orthophosphates as manifested by cathodoluminescence were investigated. New information was obtained that can be applied to the analysis of complex ceramics that contain monazite as a constituent phase.

Collaboration Type: Program interaction *Collaborator:* Dr. John M. Hanchar
Collaborating Organization: University of Notre Dame, Department of Civil Engineering and Geological Sciences, Notre Dame, IN. (BES project)

Description: To investigate the role of radiation damage in perovskite and pyrochlore phases that are constituents of titanate (SYNROC)-type ceramics for Pu disposal, techniques for the growth of pyrochlore single crystals were developed, and TEM and RBS studies of radiation effects in perovskites and pyrochlores were carried out. New insight into the radiation resistance of pyrochlore and perovskite phases has been obtained.

Collaboration Type: Program interaction *Collaborator:* Dr. W. J. Weber
Collaborating Organization: Battelle Pacific Northwest Laboratory, Richland, WA. (EMSP Project 54672)

Description: To investigate the role of radiation damage in altering potential media for the disposition of Pu and other actinides, heavy particle radiation damage experiments were performed, and the damage effects were characterized using TEM, electron diffraction, and other techniques. The experimental results formed the basis for a new model that can be used to predict wasteform stability in the case of Pu storage.

Collaboration Type: Program interaction *Collaborator:* Prof. R. C. Ewing
Collaborating Organization: Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI

Project: 55103

Title: Utilization of Kinetic Isotope Effects for the Concentration of Tritium
PI: Dr. Gilbert M. Brown *Institution:* Oak Ridge National Laboratory

Description: The objective of our work is to develop an electrochemically-based, cyclic process which can be used to remove tritium from contaminated water. We are developing methods for concentrating tritium from water based on large primary kinetic isotope effects in catalytic redox processes. H-T discrimination occurs in an oxidation step involving a transition metal oxidant and small organic compounds containing oxidizable C-H or C-T bonds. Tritium is incorporated in the organic compound by an electrochemical reduction process in the presence of tritium contaminated water, but the protio-derivative is kinetically favored in the oxidation half-reaction. As a result of a cyclic oxidation-reduction process, tritium is enriched in the organic compound. The organic compound is chosen so that it does not readily exchange the tritium with groundwater.

Collaboration Type: Consulting *Collaborator:* C.H. Ho, Douglas J. Lemme, Leon Maya, and Frederick V. Sloop, Jr.; Poonam M. Narula and Thomas J. Meyer

Collaborating Organization: ORNL, University of North Carolina at Chapel Hill

Project: 55110

Title: An Alternative Host Matrix Based on Iron Phosphate Glasses for the Vitrification of Specialized Nuclear Waste Forms

PI: Dr. Delbert E. Day *Institution:* University of Missouri-Rolla

Description: Certain high level wastes (HLWs) are not well suited for vitrification in borosilicate (BS) glasses because they contain components such as phosphates that are poorly soluble in a BS host matrix. The waste loading must be significantly reduced if one is to successfully vitrify such problematic wastes in a BS glass. Iron phosphate glasses offer a technically feasible and cost effective alternative to borosilicate glasses for vitrifying such HLWs. The main objective of the project was to investigate the atomic structure-property relationships, and glass forming and crystallization characteristics, of these iron phosphate glasses and glasses containing nuclear waste components. Other physical properties such as density and thermal expansion were studied. Collaborations for each associated task are as follows: Task: X-Ray Absorption Spectroscopy (EXANES/EXAFS) at the Stanford Synchrotron Radiation Laboratory• Drs. David Shuh, Jerry Bucher, N.M. Edelstein, and Corwin Booth, Lawrence Berkeley National Laboratory Dr. Pat Allen, Lawrence Livermore National LaboratoryTask: Neutron and High Energy X-Ray Scattering Drs. Marie-Louise Saboungi, Yaspal Badyal, and Dean Heaffner, The Division of Materials Science, Intense Pulsed Neutron Source, and The Advanced Photon Source, Argonne National LaboratoryTask: Raman Spectroscopy. Dr. Marcos Grimsditch, Division of Materials Science, Argonne National Laboratory. Dr. Andrea Mogus-Milankovic, Ruder Boskovic Institute, CroatiaTask: Electron Spin Resonance Studies• Dr. David Griscom, Naval Research LaboratoryTask: Electrical properties (conductivity, loss, and dielectric constant). Dr. Andrea Mogus-Milankovic, Ruder Boskovic Institute, Croatia.

Collaboration Type: Program interaction *Collaborator:* (see description)

Collaborating Organization: (see description)

Project: 55205

Title: A Fundamental Study of Laser-Induced Breakdown Spectroscopy Using Fiber Optics for Remote Measurements of Trace Metals

PI: Dr. Scott Goode *Institution:* University of South Carolina

Description: Improved technologies are required by DOE for characterization and monitoring for site clean-up and waste processing applications. Especially needed are field deployable methods and devices of real-time monitoring. Matrices of interest to the DOE are soils, slurries, and aqueous and non-aqueous solutions. Laser-induced breakdown spectroscopy (LIBS) is a useful method for determining the elemental composition of solids. The objective of this project is to determine the optimal excitation and collection conditions and sampling times for metal contaminants in different matrices, and an understanding of the strengths and limitations of using fiber optics for LIBS sampling. PI is in the process of establishing a collaboration with EMSL.

Collaboration Type: Unclassified

Collaborating Organization: EMSL

Project: 55229

Title: The NOx System in Nuclear Waste

PI: Dr. Dan Meisel *Institution:* University of Notre Dame

Description: This project, a collaborative ANL/PNNL effort, studies processes of the title system as it relates to the chemistry in high level liquid nuclear waste (HLW). The program is structured to transfer the information directly to the Hanford site operators (via “Organic Aging Studies, PI: Don Camaioni, PNNL). Our activity is also closely coordinated with another EMSP project (“Interfacial Radiolysis”, PI: Thom Orlando, PNNL) and we include below our results that relate directly to that project. We determined the redox potential of the NO32- radical and its possible conversion to NO radical rather than to NO2. We also determined the redox potential of the analogous NO22- radicals because this parameter will determine whether such a conversion is possible. We concluded that both NO2 and NO radicals are important intermediates in HLW and the relative importance will depend on the concentration of nitrite in the waste tank. As a consequence we will coordinate our activity with a recently awarded EMSP project that focuses on NO chemistry and its derivatives (“Reactivity of Peroxynitrite”, PI: Sergei Lymar, BNL).

Collaboration Type: Mission directed *Collaborator:* Sergei Lymar, Thom Orlando

Collaborating Organization: BNL, PNNL

Project: 55264

Title: High Resolution Definition of Subsurface Heterogeneity for Understanding the Biodynamics of Natural Field Systems: Advancing the Ability for Scaling to Field Conditions

PI: Dr. Ernest L. Majer *Institution:* Lawrence Berkeley National Laboratory

Description: The objectives for this project were to develop and apply high-resolution seismic imaging methods for defining physical parameters (lithology, fracture content, fast paths, faults, etc.) that may be controlling flow and transport in naturally heterogeneous material. A primary aspect of the project was to determine if seismic imaging methods could resolve the details necessary to understand the physical heterogeneity controlling microbial behavior. Collaborations are with PNNL and INEEL. PNNL is collaborating in correlating the bacterial behavior to the zones of high permeability detected with the geophysics. INEEL provided the site (TAN) and drilling support as well as collaboration with other EMSP researchers (Colwell and Smith) in understanding the in-situ flow and microbial properties. There were also close collaborations with on site contractors (L. Peterson and T. Woods) in the collection and processing of the data.

Collaboration Type: Consulting *Collaborator:* Dr. Ardeth Simmons, LBL Yucca Mountain PM

Collaborating Organization: Yucca Mountain Project

Project: 55267

Title: Containment of Toxic Metals and Radionuclides in Porous and Fractured Meda*:* Optimizing Biogeochemical Reduction Versus Geochemical Oxidation

PI: Dr. Philip M. Jardine *Institution:* Oak Ridge National Laboratory

Description: The purpose of this research is to provide an improved understanding and predictive capability of the mechanisms that allow metal-reducing bacteria to be effective in the bioremediation of subsurface environments contaminated with toxic metals and radionuclides. The study is motivated by the likelihood that subsurface microbial activity can effectively alter the redox state of toxic metals and radionuclides so that they are immobilized for long time periods.The overall goal of this project is to use basic research to develop a cost effective remediation strategy that employs in situ contaminant immobilization. Specifically, we will develop active biowall technologies to contain priority EM contaminant plumes in groundwater. Interaction with several other EMSP projects with regard to technology transfer, data sharing, and collaboration on experimental designs.

Collaboration Type: Program interaction *Collaborator:* Dr. Eric Roden (EMSP Project 55164) and Dr. Lenly Weathers (EMSP Project 55071)

Collaborating Organization: University of Alabama and Tennessee Technological University

Project: 55318

Title: Improved Analytical Characterization of Solid Waste Forms by Fundamental Development of Laser Ablation Technology

PI: Dr. Richard E. Russo *Institution:* Lawrence Berkeley National Laboratory

Description: DOE Materials Disposition Program is developing two laser ablation systems, at SRS and LLNL for Pu characterization. Because of the reputation of the PI and the EMSP program, Russo was asked to help develop the systems and standards for this PuO2 effort.
Collaboration Type: Consulting *Collaborator:* Chris Bannochie
Collaborating Organization: DOE Savannah River

Description: This project has continuing interaction with other EMSP investigator studying laser ablation. This include projects 55205 - A Fundamental Study of Laser-Induced Breakdown Spectroscopy Using Fiber Optics for Remote Measurements of Trace Metals, and 60283 - Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation.
Collaboration Type: Program interaction *Collaborator:* Dr. Scott Goode and Dr. Michael J. Pellin
Collaborating Organization: USC and Argonne National Laboratory

Description: Characterization continues to be a need within the DOE EM program in the areas of high-level waste, tanks, sub-surface contaminant plumes, D&D activities, spent nuclear fuel, mixed wastes, and plutonium disposition. Laser ablation can provide direct characterization of any solid waste form in a timely manner and at a reduced cost compared to conventional analytical dissolution procedures. The primary technical difficulties hindering this technology are matrix dependence and fractionation, both effect accuracy of quantitative characterization. These issues must be understood on a fundamental level to develop laser ablation as a routine characterization technology. Understanding these fundamental issues is the basis of the EMSP project. The PI has established an interaction with the primary personnel responsible for setting up the laser ablation inductively coupled plasma - mass spectroscopy (LA-ICP-MS) system in Building 222S at PNNL. The PI has visited the Hanford Site and toured the LA facility.
Collaboration Type: Consulting *Collaborator:* John Hartman, Mike Alexander, and Monte Smith
Collaborating Organization: PNNL

Project: 55388

Title: Stable Isotopic Investigations of In Situ Bioremediation of Chlorinated Organic Solvents
PI: Dr. Neil C. Sturchio *Institution:* Argonne National Laboratory

Description: The purpose of this project was to investigate the potential applications of stable isotope ratio measurements in characterization of the source terms, the transport, and the fate of chlorinated solvents in groundwater aquifers. The approach to this research was threefold: to develop methods for the sampling and isotopic analysis of chlorinated solvents in groundwaters; to perform laboratory experiments to measure equilibrium and kinetic isotope effects associated with biological and physical transformation processes of chlorinated solvents; and to perform field investigations at well-characterized, contaminated aquifer sites to demonstrate the applicability of the isotopic approach in real-world situations. To further these means the following collaborations were established: - Mr. Jay Clausen (Lockheed-Martin Energy Systems, Inc., Kevil, KY (now at Ogden Energy and Environmental Systems, Inc., Westport, MA), on application of chlorine isotope ratio measurements in an investigation of natural attenuation of trichloroethene at the Paducah Gaseous Diffusion Plant.- Mr. Greg Smith, ENSR, Inc. (now at Radian International), on application of carbon and chlorine isotopic measurements to solvent cleanup activities at a number of industrial sites.- Dr. Chris Reddy, Woods Hole Oceanographic Institute, Woods Hole, MA, on application of chlorine isotope measurements to environmental studies of semivolatile.

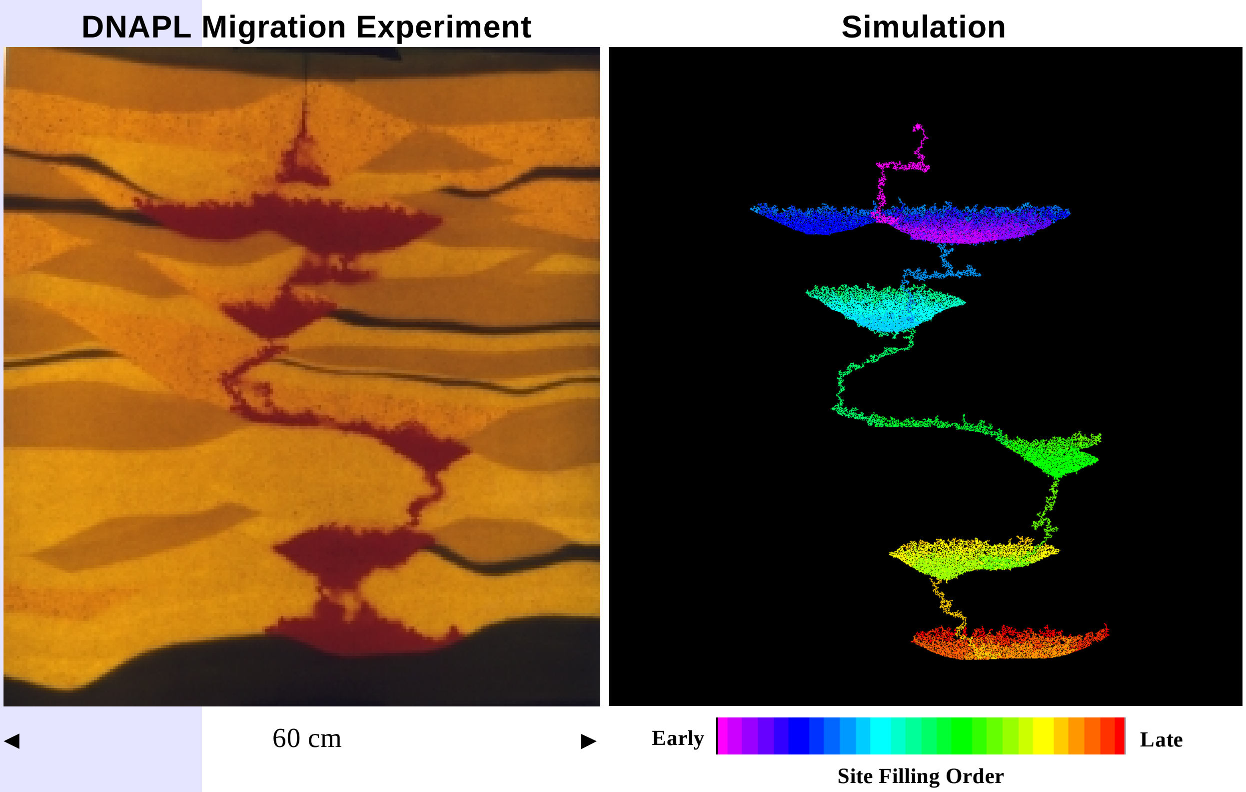
Collaboration Type: Mission directed *Collaborator:* (see description)
Collaborating Organization: (see description)

Project: 55395

Title: Physics of DNAPL Migration and Remediation in the Presence of Heterogeneities

PI: Dr. Stephen H. Conrad *Institution:* Sandia National Laboratories

Description: For our MA surfactant experiment, we obtained surfactant advice from Alex Meyer and Lirong Zhong. The experiment used the surfactant MA and was designed to maximize solubilization while minimizing mobilization.



Results of a DNAPL migration experiment conducted at Sandia National Laboratories are compared to upscaled percolation modeling. The photo (left) illustrates that the DNAPL(dyed red) migrated downward due to its high density but that aquifer heterogeneities caused significant pooling along the migration path. DNAPL in such a configuration served as the initial condition for remediation experiments. The simulation image (right) compares extremely well with the experiment. [see Project #55395]

Contrary to expectation, we observed dramatic mobilization. The DNAPL penetrated the aquitard and became inaccessible to the surfactant. Even though trapping number calculations predict some modest amount of mobilization, failure to account for DNAPL in pools resulted in significantly underestimating the potential for extensive downward mobilization. In observing the mobilization process, we discovered a previously unknown mobilization process that occurs when the surfactant front first encounters a pool. Very different interfacial tensions on either side of the surfactant front result in enhanced drainage of the DNAPL pool. For our particular experimental conditions, due to downward mobilization and penetration of the DNAPL into fine-grained units, introduction of the MA surfactant actually made the problem worse.

Collaboration Type: Consulting *Collaborator:* Dr. Alex Meyer and Lirong Zhiong
Collaborating Organization: Michigan Tech

Description: For the Tween surfactant experiment, we obtained surfactant advice from Dr. Kurt Pennell, a professor at Georgia Tech. We obtained much better results using the Tween surfactant. We observed only modest DNAPL mobilization because the Tween surfactant maintains a much higher water/organic interfacial tension. We also observed good solubilization. Complete cleanup was achieved after several pore volumes of flushing. Time lapse animation of this experiment yielded important insights into remediation .

Collaboration Type: Consulting *Collaborator:* Dr. Kurt Pennell
Collaborating Organization: Georgia Tech

Description: We worked with Dr. Varadarajan Dwarakanath of Duke Engineering to design the tracer test. It occurred to us that the certain conditions provided by our remediation experiments – subsequent to the emplacement if the DNAPL and prior to beginning the remediation – were ideal for performing a tracer test while requiring very little extra work. Partitioning tracer tests are designed to compare the breakthrough of partitioning and non partitioning tracers. Retardation of the tracers that partition into the organic phase provides a means to calculate the mass of DNAPL contained in the region swept by the tracer test. We found that the test worked qualitatively, indicating the presence of DNAPL, but the calculations significantly underestimated the mass of DNAPL in the chamber. We believe that failure to account for the fact that the vast majority of the DNAPL mass existed in large pools resulted in under-prediction of DNAPL mass. When significant DNAPL mass exists in pools, typical tracer flow rates do not allow sufficient time for partitioning/diffusion of the tracers into and out of large pools.

Collaboration Type: Consulting *Collaborator:* Dr. Varadarajan Dwarakanath
Collaborating Organization: Duke Engineering

Description: For the Permanganate experiment, we worked with Dr. Jack Istok, a professor at Oregon State. Flushing with potassium permanganate has been investigated as an oxidizer that mineralizes TCE. Jack suspected that the manganese precipitate that forms as a mineralization product cause permeability reduction and thereby inhibit access between the TCE and the permanganate solution and this is precisely what we were able to visually observe in this experiment. The manganese precipitate formed a low permeability rind surrounding the DNAPL pools. Such results had not been seen previously, because for experiments run in uniform media, the DNAPL does not reside in pools. The permanganate oxidation process not likely to be as efficient as initially hoped in cases where DNAPL resides in pools. Perhaps intermittent flushes with a substance to dissolve away manganese precipitate might be possible.

Collaboration Type: Consulting *Collaborator:* Dr. Jack Istok
Collaborating Organization: Oregon State

Description: The project involves conducting well-controlled laboratory experiments to better understand the physics of DNAPL migration and remediation in the presence of heterogeneities. The results will be used to test and to continue development of new modeling approaches. In addition, the results of the remediation experiments will be used to test the quantitative performance of remediation design codes within heterogeneous media. We intend to work closely with developers of each remediation approach to attempt to optimize the remedial process and show each technique in its best possible light. Towards that end, Alex Meyer, a professor at Michigan Tech, visited our lab and is collaborating with us on our first series of experiments looking at surfactant mobilization and solubilization of DNAPLs.

Collaboration Type: Consulting *Collaborator:* Dr. Alex Meyer
Collaborating Organization: Michigan Tech

We are using an array of 50 outdoor mesocosms to address ecological risk questions. The mesocosm facility allows us to conduct replicated, controlled dose-effect studies on biota under continuous low-level exposure conditions. This photo shows thermoluminescent dosimeters placed within a mesocosm to test the homogeneity of the radiation exposure field. [see Project #55410]

Project: 55410

Title: Determining Significant Endpoints for Ecological Risk Analysis
PI: Dr. Thomas G. Hinton
Institution: Savannah River Ecology Laboratory

Description: Our interest is in obtaining a scientifically defensible endpoint for measuring ecological risks to populations exposed to chronic, low-level radiation, and radiation with concomitant exposure to chemicals. To do so, we believe that we must understand the extent to which molecular damage is detrimental at the individual and population levels of biological organization. Ecological risk analyses based on molecular damage, without an understanding of the impacts to higher levels of biological organization, could cause cleanup strategies on DOE sites to be overly conservative and unnecessarily expensive. The PI has taken knowledge gained from this research and used it in his work with the DOE Biota Dose Assessment Group (BDAG). BDAG is currently reviewing ecological risk concepts and establishing guidelines for conducting ecological risks on DOE Facilities.

Collaboration Type: Consulting
Collaborator: Dr. Thomas Hinton
Collaborating Organization: Savannah River Ecology Lab - University of Georgia

Project: 55416

Title: Control of Biologically Active Degradation Zones by Vertical Heterogeneity: Applications in Fractured Media
PI: Dr. Frederick S. Colwell
Institution: Idaho National Engineering and Environmental

Description: The DOE is faced with cleaning up wastes from reactor and weapons production activities during the last fifty years. Many DOE sites have contaminants that are difficult to access due to depth and complex geology and are challenging to degrade using conventional methods. The key objective of this project is to determine the distribution of biologically active contaminant degradation zones in a fractured, subsurface medium with respect to vertical heterogeneities.
Collaboration Type: Consulting
Collaborator: Lance Peterson, Kent Sorenson, and Joe Rothermel
Collaborating Organization: Idaho National Engineering and Environmental Laboratory

Aseptic sampling of fractured rock. [see Project #55416]

Project: 59849

Title: Radionuclide Immobilization in the Phases Formed by Corrosion of Spent Nuclear Fuel: The Long-Term Assessment
PI: Dr. Rodney C. Ewing
Institution: University of Michigan

Description: Continued efforts to evaluate the capabilities of the uranyl phases to incorporate and retard release of important radionuclides: Np-237, Se-79, Tc-99, and I-129.
Collaboration Type: Program interaction
Collaborator: Professor Peter Burns *Collaborating Organization:* Notre Dame

Description: In the area of spent nuclear fuel corrosion, we maintain an active program of collaborations with the following individuals: Dr. Peter Burns, Notre Dame University- structural studies and refinements of uranium mineralsDr. Jordi Bruno, QuantiSci, Barcelona, Spain- leaching studies of uranium minerals; solution chemistry of actinidesDr. Ignasi Casas, Department of Chemistry, UPC, Barcelona, Spain- leaching studies of uranium mineralsDr. Fanrong Chen, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, P.R. China - geochemical modeling of uranium-phase dissolutionProfessor Sue Clark, Department of Chemistry Washington State University- structure-based models of solubilityDr. Mostafa Fayek, Center of Isotope Geochemistry, Oak Ridge National Laboratory- isotopic studies of uranium depositsProfessor Frank Hawthorne, Department of Geological Sciences, University of Manitoba- crystal structure refinements of uranium mineralsProfessor Hiroshi Hidaka, Department of Earth And Planetary Systems Science, Hiroshima University- SIMS analysis of uranium-bearing phasesProfessor Janusz Janeczek, Faculty of Earth Sciences, University of Silesia- mineralogy and geochemistry of the Oklo reactorsProfessor Takashi Murakami, Mineralogical Institute, Tokyo University- studies of uranium phases by FEG-TEM and x-ray diffraction analysisDr. Juan de PabloDepartment of Chemical Engineering UPC, Barcelona, Spain- leaching studies of uranium minerals.

Collaboration Type: Program interaction
Collaborator: (see description)
Collaborating Organization: (see description)

Radon thoron detector, as it would be used in the field of personal monitoring. [see Project #59882]

Project: 59882

Title: Measurements of Radon, Thoron, Isotopic Uranium and Thorium to Determine Occupational & Environmental Exposure & Risk at Fernald Feed Materials Production Center.
PI: Dr. Naomi H. Harley
Institution: New York University Medical School

Description: One objective of this project is to develop the sequential radiochemistry necessary to measure any environmental sample for the isotopes of uranium, thorium, radium and lead-210. To utilize this radiochemistry for lead-210 before and after the radium is removed form the silos to accurately determine the amount of radon gas released, from the parent radium during removal. To utilize the radiochemistry to accurately trace and delineate thorium, radium and uranium nuclides, originating from Fernald, in the environment. Dr. Fisenne at USDOE Environmental Measurements Laboratory has developed a sequential radiochemical procedure to analyze any environmental sample matrix, presently focused on Soil samples, for Lead-210, radium, thorium, and uranium isotopes. We are currently cunsulting with Dr. Fisenne.

Collaboration Type: Consulting *Collaborator:* Dr. Isabel Fisenne
Collaborating Organization: Environmental Measurements Laboratory

Project: 59918

Title: Improved Radiation Dosimetry/Risk Estimates to Facilitate Environmental Management of Plutonium Contaminated Sites

PI: Dr. Bobby R. Scott *Institution:* Lovelace Biomedical & Environmental Research

Description: We are now assisting staff at the Rocky Mountain Remediation Services, L.L.C., Rocky Flats Environmental Technology Site in preparing a scientifically valid approach to selecting respiratory protection devices for use in very high concentrations of plutonium. Some concentration of interest would essentially lead to early occurring or delayed deaths without adequate worker protection. The activities at Rock Flats relate to decontamination and decommissioning. Our staff reviewed an original draft white paper related to selecting appropriate respiratory devices and major shortcomings related to protecting DOE decontamination/decommissioning workers were pointed out. We will continue to assist in preparing a more credible plan for protecting workers and in preparing an associated white paper.

Collaboration Type: Consulting *Collaborator:* Rocky Mountain Remediation Services, L.L.C.,

Collaborating Organization: Rocky Flats Environmental Technology Site

Description: Additional data on lung cancer induced in Mayak workers exposed by inhalation to both plutonium and cigarette smoke were acquired by Dr. Scott from scientists at the Branch No. 1 of the Institute of Biophysics, Ozersk Russia. The data will facilitate making conclusions about possible interactions between alpha radiation and cigarette smoke in the induction of lung cancer. The data will also allow for additional insights to be made related to the validity of the linear, no-threshold hypothesis for cancer induction.

Collaboration Type: Mission directed *Collaborator:* Unknown

Collaborating Organization: Branch No. 1 of the Institute of Biophysics, Ozersk Russia

Project: 59934

Title: Hazardous Gas Production by Alpha Particles in Solid Organic Transuranic Waste Matrices

PI: Dr. Jay A. LaVerne *Institution:* University of Notre Dame

Description: Hazardous gas production by the self-radiolysis of solid organic matrices, such as polymers and resins, containing radioactive material is a serious problem for waste management. Hydrogen is the most common hazardous gaseous product, although methane and ethane are possible, depending on the particular material. The yield of these products can be an order of magnitude different between alpha particles and gamma rays. Studies are in progress to estimate hazardous gas production in various solid matrices with different radiation. Fundamental knowledge on radiation chemical processes is being transferred to interested researchers at Los Alamos National Laboratory.

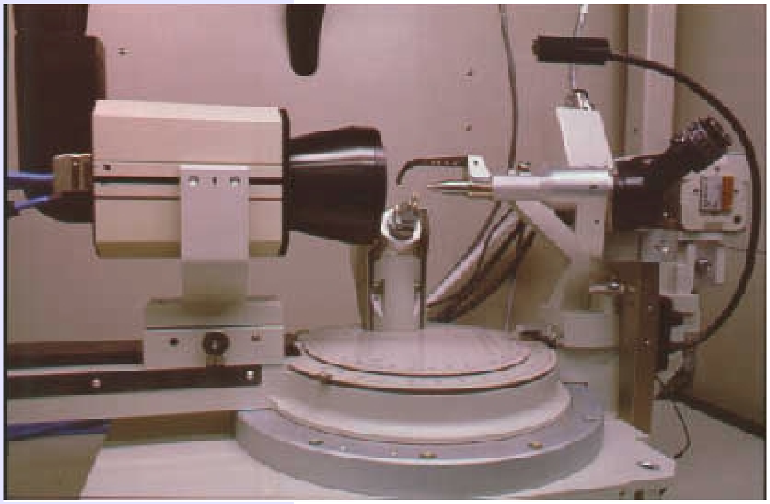
Collaboration Type: Consulting

Collaborating Organization: Los Almos National Laboratory

Project: 59960

Title: Direct Investigations of the Immobilization of Radionuclides in the Alteration Phases of Spent Nuclear Fuel

PI: Dr. Peter C. Burns *Institution:* University of Notre Dame



The CCD-based X-ray diffraction system used to determine the structures of many uranyl phases. [see Project #59960]

Description: The National Spent Nuclear Fuels Program (NSNFP) is interested in this research concerning the mobility of the radionuclides in Spent Nuclear Fuels (SNF) for their work on the repository at Yucca Mountian. Dr. Burns is collaborating with ANL-E, where they are performing drip tests in a hot cell on commercial SNF. Ms. Davis has a work package funded by the NSNFP which funds ANL-E to perform similar release rate testing on DOE SNF. She is interested in having Dr. Burns perform an analysis on DOE SNF, similar to what he has done on commercial SNF. Dr. Paul Lessing is investigating the incorporation of Gadolinium as a neutron absorber into the DOE SNF packages which will be sent to Yucca Mountian. He would be interested in having Dr. Burns investigate the mobility of Gd in SNF packages.

Collaboration Type: Mission directed

Collaborator: Colleen Shelton-Davis

Collaborating Organization: National Spent Nuclear Fuels Program

An SEM image of a new uranyl silicate phase found growing on actinide-bearing borosilicate wasteglass (S51) from Savanna River. The glass was placed in 100% humidity at 200?C for 60 days. This phase is new to science. The crystal structure was determined using X-ray diffraction, and obtained chemical analysis with an electron probe. This phase is potentially a very important sink for actinides where waste forms are altered under repository conditions. [see Project #59960]

Description: In an oxidizing environment, such as the proposed repository at Yucca Mountain (YM), rapid alteration rates are expected for spent nuclear fuel. Laboratory-scale simulations demonstrate that the dominant alteration products under YM repository conditions will be uranyl phases. There is an inadequate database to relate the effects of alteration products to the release of radionuclides, although this information is essential for providing realistic radionuclide-release estimates. It is likely that many radionuclides contained in spent fuel will be incorporated into alteration products with a potentially profound impact on the future mobility of radionuclides in the repository. Our objective is to characterize the incorporation of radionuclides into U(VI) alteration products by synthesizing uranyl phases doped with radionuclides, appropriate surrogate elements, or non-radioactive isotopes, followed by detailed phase characterization by diffraction and spectroscopic techniques.

This research will permit a more realistic estimate of the release rates of radionuclides from the repository's near-field environment.In collaboration with Rudolph Olson of Argonne National Laboratory, we solved the crystal structure of a novel uranyl silicate formed during the corrosion of an actinide-bearing waste glass. The structure contains sheets of eight- and four-membered silicate tetrahedral rings, linked together by uranyl square bipyramids. Channels within the uranyl silicate framework are occupied by low valence cations including K and Na, as well as water molecules. We expect this phase to form under YM repository conditions.

Collaboration Type: Program interaction
Collaborator: Rudolph Olson
Collaborating Organization: ANL

Project: 60020

Title: Stability of High-Level Waste Forms
PI: Dr. Theodore M. Besmann *Institution:* Oak Ridge National Laboratory

Description: Experimental studies of phase relations in the sodium oxide-boron oxide-uranium (VI) oxide system are being run in this EMSP program because there is no information in the literature. This data is needed for modeling actinide behavior in glasses. The results of these tests are also being spun off to assist the Uranium-233 Disposition Program of the Office of Fissile Materials Disposition (DOE/MD). They are considering dissolution of uranium oxide in sodium borate or boron oxide as an option for Uranium-233 disposition. As experimental data is produced, it is made available to the Uranium-233 Program to assist in their development of a flow sheet. Because of the dearth of information on this system, it is not surprising that any information that is produced may be applied in different activities.

Collaboration Type: Joint interaction *Collaborator:* Charles Forsberg
Collaborating Organization: ORNL

Description: Models of phase relations and liquidus temperatures developed in this EMSP program are being used to evaluate test results from the Tanks Focus Area Immobilization Program "Waste Loading Improvements in High and Low Activity Glasses and Waste Form Product Acceptance Testing." The focus at this time is on conditions where crystallization occurs in glass processing. By applying models to the test data, an understanding of crystallization and how to avoid it may be obtained.

Collaboration Type: Joint interaction *Collaborator:* John Vienna
Collaborating Organization: PNNL

Description: The objective of the project is to use a new approach to develop solution models of complex waste glass systems and spent fuel that are predictive with regard to composition, phase separation, and volatility. We have been supporting efforts on increasing waste loading in glass. We have performed computations modeling a waste glass formulation to predict precipitation of a crystalline phase, nepheline, which destabilizes the glass. The results indicated compositional regions that promoted or suppressed precipitation. These can be used to help design glass compositions that will allow increased waste loading.

Collaboration Type: Consulting *Collaborator:* John Vienna, Pavel Hrma, and Hong Li

Collaborating Organization: TFA Immobilization Project (PNNL)

Project: 60069

Title: Least-Cost Groundwater Remediation Design Using Uncertain Hydrogeological Information

PI: Dr. George F. Pinder *Institution:* University of Vermont

Description: The project seeks to examine the importance of uncertainty in hydraulic conductivity in the least-cost design of groundwater contamination containment systems. The project uses a new conceptual approach to accommodate aquifer parameter uncertainty in optimal groundwater remediation design and introduces a new operations-research technique to solve the optimization problem. The new approach, Robust Optimization, allows for the determination of a robust, lowest-possible cost, pumping design that is consistent with the inherent uncertainty in the hydraulic conductivity field. It also allows for the visualization of how one can trade off excess pumping for enhanced security. Collaborated with BNL for a review of Brookhaven groundwater contamination.

Collaboration Type: Consulting

Collaborating Organization: BNL

Project: 60075

Title: Particle Generation by Laser Ablation in Support of Chemical Analysis of High Level Mixed Waste from Plutonium Production Operations

PI: Dr. J. Thomas Dickinson *Institution:* Washington State University

Description: We have been working with Dr. Beverly Crawford. Dr. Crawford is in charge of a laser ablation ICP-MS system that has been installed in a hot cell in the Hanford 222S building. One of the key technical questions is how well laser ablation can determine the overall bulk composition of a heterogeneous sample given a small volume of material sampled. We have begun to address the homogeneity issue .

Collaboration Type: Joint interaction *Collaborator:* Jim Rindfleisch

Collaborating Organization: Long Range Waste Management Program, INEEL

Description: Performing laser ablation/description analytical determination on a surrogate sample. Contacted Arlin Olson and Scott Herbst to identify the surrogate and analytical requirements. Investigate analysis of these samples by laser ablation IMP-MS as well as a related method, laser desorption mass spectroscopy to determine key molecular components. The goal is to generate a complete mass balance of the calcine waste.

Collaboration Type: Joint interaction *Collaborator:* Dr. Beverly Crawford

Collaborating Organization: Numatec, Hanford

Project: 60077

Title: Development of Nuclear Analysis Capabilities for DOE Waste Management Activities

PI: Dr. Cecil V. Parks *Institution:* Oak Ridge National Laboratory

Description: The objective of this project is to develop and demonstrate prototypical analysis capabilities that can be used by nuclear safety analysis practitioners to: (1) provide a more thorough understanding of the underlying physics phenomena that can lead to improved reliability and defensibility of safety evaluations; and (2) optimize operations related to the handling, storage, transportation, and disposal of fissile material and DOE spent fuel. To address these problems, this project will investigate the implementation of sensitivity and uncertainty methods within existing Monte Carlo codes used for criticality safety analyses, as well as within a new deterministic code that allows for specification of arbitrary grids to accurately model geometric details required in a criticality safety analysis. A study of the application of sensitivity and uncertainty methodology to relevant EM problems of current interest was conducted. With the help of Michaele Brady Raap at Hanford and Todd Taylor at INEEL, ORNL researchers reviewed applications related to the tank farms and disposal of spent nuclear fuel to assess the potential changes in safety margin that might be achieved using the sensitivity and uncertainty methodology.

Collaboration Type: Program interaction *Collaborator:* Michaele Brady Rapp (Hanford) and Tood Taylor (INEEL)

Collaborating Organization: DOE Nuclear Criticality Safety Program

Project: 60118

Title: Fundamental Thermodynamics of Actinide-Bearing Mineral Waste Forms

PI: Dr. Mark A. Williamson *Institution:* Argonne National Laboratory

Description: The end of the Cold War raised the need for the technical community to be concerned with the disposition of excess nuclear weapon material. The plutonium will either be converted into mixed-oxide fuel for use in nuclear reactors or immobilized in glass or ceramic waste forms and placed in a repository. The stability and behavior of plutonium in the ceramic materials as well as the phase behavior and stability of the ceramic material in the environment is not well established. The purpose of this project is to determine the thermodynamic data essential to developing an understanding of the chemistry and phase equilibria of the waste form materials proposed as immobilization matrices. Collaboration with DOE-MD program for Dispositioning of Plutonium by Immobilization.

Collaboration Type: Program interaction

Collaborating Organization: DOE-MD

Project: 60143

Title: Foaming in Radioactive Waste Treatment and Immobilization Processes
PI: Dr. Darsh T. Wasan *Institution:* Illinois Institute of Technology

Description: Illinois Institute of Technology (IIT) has been working closely with the Savannah River Technology Center in the development of an improved antifoaming agent for the Defense Waste Processing Facility (DWPF). The key to the development of this new antifoam agent was a close working relationship between the IIT researchers and the customer (Dan Lambert) at the Savannah River Site (SRS). University and national lab researchers often come up with unique and innovative solutions that are useless to the customer. The reason for the success of this project can be attributed to the fact that the IIT researchers sought to understand the science and the limitations in the customer's waste processing facility through close working relationships.
Collaboration Type: Mission directed
Collaborating Organization: Savannah River Technology Center

Project: 60144

Title: Flow Visualization of Forced and Natural Convection in Internal Cavities
PI: Dr. John C. Crepeau *Institution:* University of Idaho

Description: The goal of this program is to develop innovative flow visualization methods and predictive techniques for energy, mass and momentum transfer in the presence of chemical reactions in the drying and passivation of spent nuclear fuel (SNF) elements. Efforts on this project are coordinated with the National Spent Nuclear Fuel programs. Their staff have provided guidance on the wide range of SNF canister configurations and fuel elements in use; from this information this EMSP project has developed the descriptions of generic flow processes of concern and, thereby, designed the experiments conducted. The SNF staffs have provided understanding of needs for fundamental studies and have reviewed project results and plans for our fundamental studies.
Collaboration Type: Mission directed
Collaborating Organization: National Spent Nuclear Fuel programs

Project: 60219

Title: Development of Advanced Electrochemical Emission Spectroscopy for Monitoring Corrosion in Simulated DOE Liquid Waste
PI: Dr. Digby D. MacDonald *Institution:* Pennsylvania State University

Description: The principal goals of this project are to develop advanced electrochemical emission spectroscopic (EES) methods for monitoring the corrosion of carbon steel in simulated DOE liquid waste and to develop a better understanding of the mechanisms of the corrosion of metals and alloys in these environments. To faciliate this goal, interaction with SRI International has been begun.
Collaboration Type: Joint interaction *Collaborator:* Dr. George Engelhardt
Collaborating Organization: SRI International

Project: 60283

Title: Waste Volume Reduction Using Surface Characterization and Decontamination by Laser Ablation

PI: Dr. Michael J. Pellin *Institution:* Argonne National Laboratory

Description: The waste stream generated in the D&D efforts for nuclear facilities includes a significant volume of material that is contaminated only in the surface or near-surface region. It is critical to understand the depth-dependent concentration and chemistry of radionuclide-contaminated surfaces. Complete removal and capture of the contaminated surface would greatly reduce the volume of waste material generated in, and thus the cost of, D&D efforts. This project represents the first detailed surface studies of the sorption of radionuclides in complex materials such as concrete. Collaboration is a joint interaction with Zawtech Inc. to do further research into areas of practical applications.

Collaboration Type: Joint interaction

Collaborating Organization: Zawtech Inc.

Project: 60296

Title: Research Program to Investigate the Fundamental Chemistry of Technetium

PI: Dr. Norman M. Edelstein *Institution:* Lawrence Berkeley National Laboratory

Description: This project addresses the fundamental solution chemistry of technetium (Tc) in the waste tank environment, and the stability of Tc in various waste forms. A separate facet of this project is the search for lower valent forms of Tc that may be incorporated in various waste forms for long term storage. Collaborated with PNNL as a participant (technical expert) at Technetium Chemistry workshop review panel assessing tank technetium removal/disposition options.

Collaboration Type: Consulting

Collaborating Organization: PNNL

Project: 60345

Title: New Silicotitanate Waste Forms: Development and Characterization

PI: Dr. Mari Lou Balmer *Institution:* Pacific Northwest National Laboratory

Description: In this program, we at SNL have developed both a silicotitanate ion exchanger and a new Metal Niobate Ion exchanger. Both are excellent at divalent cation selectivity. The Metal Niobate Ion Exchanger shows exceptional selectivity for divalent cations over monovalent cations. Though this is in the experimental stage (and NOT yet an optimized material), we do see great potential for this material is a variety of applications around the DOE complex. This material is currently submitted for a patent. We are in discussions with INEEL, about simulant testing of these non-optimized materials for various DOE complex wastes.

Collaboration Type: Mission directed *Collaborator:* Dean Peterman

Collaborating Organization: INEEL

Description: This project, a collaborative PNNL/SNL/UC Davis effort, identifies new waste forms and disposal strategies specific to crystalline silicotitanate (CST) secondary waste that is generated from Cs and Sr ion exchange processes. The goals of the program are to reduce the costs associated with CST waste disposal, to minimize the risk of contamination to the environment during CST processing, and to provide DOE with technical alternatives for CST disposal. The technical objectives of the proposed work are to fully characterize the phase relationships, structures and thermodynamic and kinetic stabilities of crystalline silicotitanate waste forms and to establish a sound technical basis for understanding key waste form properties, such as melting temperatures and aqueous durability, based on an in-depth understanding of waste form structures and thermochemistry. Collaborations for each associated task are as follows: Task: Evaluation of thermally converted CST and structure/ properties relationship studies of silicotitanates and related compounds - Y. Su, E. Bitten, and D. McCready, PNNL (Program interaction)Task: Hydrothermal synthesis silicotitanates and related ion exchanger material.- Nenoff and M. Nyman, SNL (Program interaction)Task: Thermochemical studies of silicotitanates and related ion exchanger materials. - A. Navrotsky and H. Xu, UC Davis (Program interaction)Task: Single crystal growth - Dr. R. Roth, NIST and The Viper Group (Consulting) Task: Radiation damage studies of silicotitanates - Professor R. Ewing, University of Michigan. (Consulting)

Collaboration Type: Consulting *Collaborator:* (see description)
Collaborating Organization: (see description)

Project: 60362

Title: Ion-Exchange Processes and Mechanisms in Glasses
PI: Dr. B. Peter McGrail *Institution:* Pacific Northwest National Laboratory

Description: The objective of this project is to develop an understanding of the processes and mechanisms controlling alkali ion exchange and to correlate the kinetics of the ion-exchange reaction with glass structural properties. The fundamental understanding of the ion-exchange process developed under this study will provide a sound scientific basis for formulating low exchange rate glasses with higher waste loading, resulting in substantial production and disposal cost savings. Collaboration with Dr. David K. Shuh at the Lawrence Berkeley National Laboratory.

Collaboration Type: Program interaction *Collaborator:* D.K. Shuh
Collaborating Organization: Lawrence Berkeley National Laboratory

Project: 60370

Title: Rational Design of Metal Ion Sequestering Agents
PI: Dr. Kenneth N. Raymond *Institution:* Lawrence Berkeley National Laboratory

Description: Provided atomic coordinates from X-Ray crystal structures of actinide complexes of hydroxypyridinone, terephthalamide and other ligands. This

data is used in high level computational studies directed toward rational design of new actinide sequestering agents.
Collaboration Type: Program interaction *Collaborator:* Dr. Ben Hay
Collaborating Organization: PNNL

Description: Synthesized and evaluated water-soluble chelating polymers, based on hydroxypyridinone and terephthalamide ligands attached to polyethyleneimine (PEI), as sequestering agents for uranyl, Pu and Am
Collaboration Type: Program interaction *Collaborator:* Drs. Barbara Smith and Gordon Jarvinen
Collaborating Organization: LANL

Description: Synthesized ligands and developed a general synthetic methods to apply a broad range of coordinating groups as actinide sequestering agents in Self-Assembled Monolayers on Mesoporous Silica.
Collaboration Type: Program interaction *Collaborator: :* Dr. Glen Fryxell
Collaborating Organization: PNNL

Description: This project addresses the fundamental issues and requirements for developing hazardous metal ion separation technologies applicable to the treatment and disposal of radioactive waste. Our research encompasses the following areas: the design and synthesis of metal ion specific sequestering ligands, structural and thermodynamic investigations of these ligand and the complexes formed with targeted metal ions, and the development and incorporation of these ligands into applied separation technologies as highly effective materials for hazardous metal ion decontamination. This interaction has provided direct structural, thermodynamic and electrochemical studies of plutonium complexes.
Collaboration Type: Program interaction *Collaborator:* Dr. Heino Nitsche
Collaborating Organization: LBNL

Project: 60403

Title: Phase Chemistry of Tank Sludge Residual Components
PI: Dr. James L. Krumhansl *Institution:* Sandia National Laboratories

Description: Because it is not possible to recover all of the contaminated sludge from the bottoms of decommissioned waste storage tanks, a credible model for the release of radionuclides from residual sludge is needed. Those sludge components most likely to retain radionuclides will be identified and synthesized. Radionuclide sorption and desorption will also be studied. AFM and STM studies will provide a firm atomistic explanation for the observed interactions between the sludge, solutions, and radionuclides. This understanding will be used to develop a quantitative radionuclide release source term for use in the performance assessment calculations. Collaboration with Larry Bustard at TFA regarding aspects of tank fluid/ sludge interactions.
Collaboration Type: Consulting *Collaborator:* Larry Bustard
Collaborating Organization: TFA

Project: 64907

Title: “Green” Biopolymers for Improved Decontamination of Metals from Surfaces: Sorptive Characterization and Costing Properties

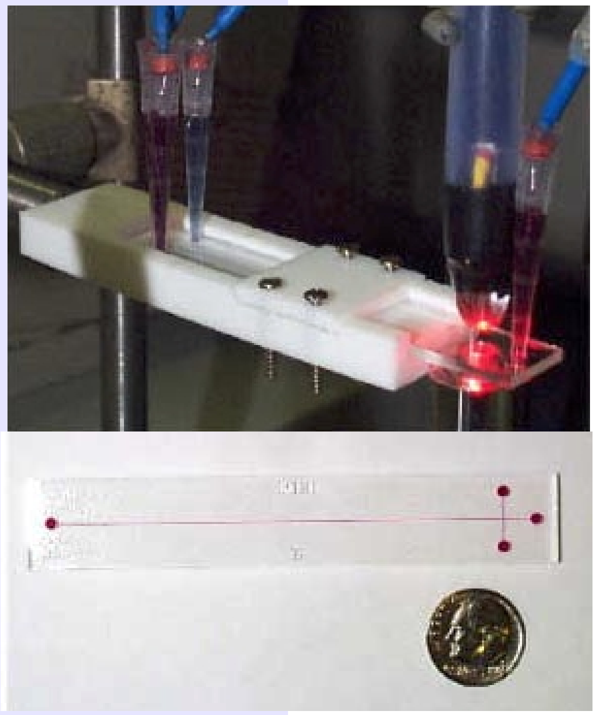
PI: Dr. Brian H. Davison *Institution:* Oak Ridge National Laboratory

Description: Entered discussions with algal biomass producers at Hebrew University, Israel and Ben Gurion University, Israel on selection and production of biopolymer. Inexpensive production of the biopolymers is essential for the ultimate application. We established contacts with several researchers and developers in growing algae in bulk. These include commercial demos of biosorption in the U.S. Collaborations in detail will need to wait for selection of a biopolymer and completion of preliminary proof-of-concept tests.

Collaboration Type: Program interaction

Collaborator: : Elisha Ter-Or and Shosham Arad

Collaborating Organization: Hebrew University and Ben Gurion University



Portable Lab-on-a-Chip Sensor for Radionuclide and Heavy Metals. [see Project #64982]

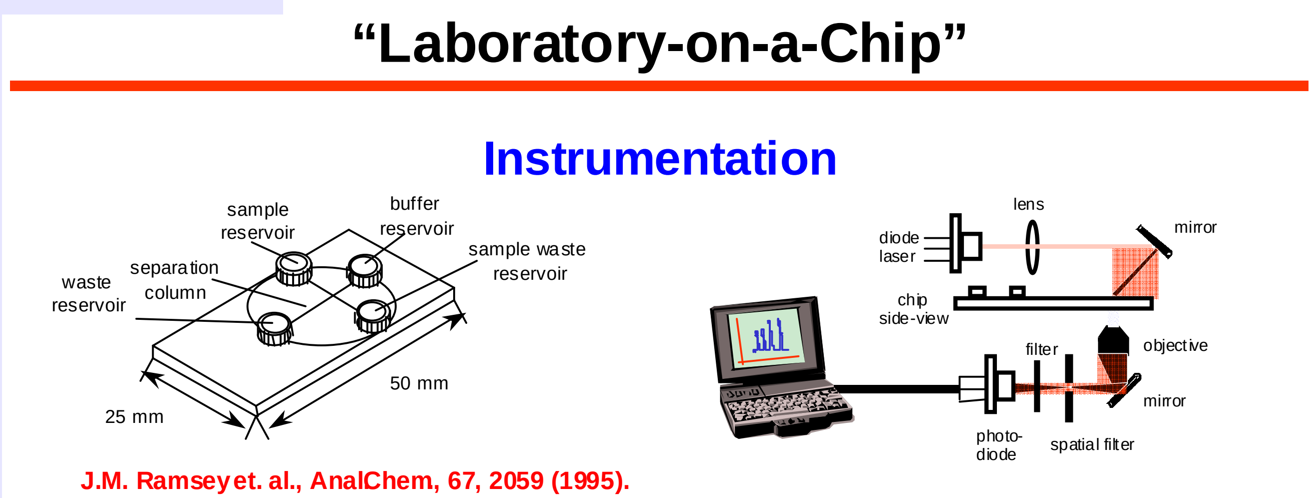
Project: 64982

Title: Metal Ion Analysis Using Near-Infrared Dyes and the “Laboratory-on-a-Chip”

PI: Dr. Greg E. Collins

Institution: Naval Research Laboratory

Description: This project addresses the need for developing a new class of radionuclide and heavy metal complexation agents that are tagged with near-infrared dyes and, therefore, can be extended to the implementation of a compact and portable “laboratory-on-a-chip” operable in the stringent field requirements of DOE site characterization and remediation. Collaboration with Dick



The Laboratory-on-a-Chip is intended to provide a field portable characterization instrument for in-situ waste characterization. [see Project #64982]

Meservey with the Decontamination and Deactivation Focus Area to refine the project direction. Commitments to support field-testing have been received.

Collaboration Type: Mission directed *Collaborator:* Dick Meservey
Collaborating Organization: DDFA

Project: 65411

Title: Precipitation and Deposition of Aluminum-Containing Phases in Tank Wastes
PI: Dr. Jun Liu *Institution:* Pacific Northwest National Laboratory

Description: Aluminum-containing phases represent the most prevalent solids that can appear or disappear during the processing of radioactive tank wastes. Of all constituents of tank waste, Al-species have the greatest potential for clogging pipes and transfer lines, fouling highly radioactive components such as ion exchangers, and completely shutting down processing operations. The primary focus of this project is to understand the major factors controlling precipitation, scale formation, and cementation of existing soluble particles by Al-containing phases. The results will be used to predict and control precipitation, scale formation, and cementation under tank waste processing conditions. The results will also provide information regarding what Al-containing phases form and how soluble such phases are in basic tank waste solutions. The project will have an important impact on waste minimization and on the retrieval, transport, and separation of tank wastes. Collaboration with Dr. Albert Hu at Lockheed Martin Hanford Company to perform simulations to support the ESP modeling work at Hanford.

Collaboration Type: Program interaction *Collaborator:* Dr. Albert Hu
Collaborating Organization: Lockheed Martin Hanford Company

Project: 65435

Title: Millimeter-Wave Measurements of High Level and Low Activity Glass Melts
PI: Dr. Paul P. Woskov *Institution:* Massachusetts Institute of Technology

Description: The developments of this project are being closely monitored by the Tanks Focus Area (TFA). A formal meeting with TFA representatives was held at Plasma Science Fusion Center, Massachusetts Institute of Technology on December 7, 1999 to discuss the transfer of the millimeter-wave-based melter diagnostics technology being developed under the EMSP project (PNNL-MIT-SRTC). The meeting was successful in identifying potential deployment of millimeter wave technology to meet the needs of the TFA. The participants of the meeting were as follows: PNNL - S. K. Sundaram MIT - Paul Woskov, Paul Thomas, Kamal Hadiddi, and John MachuzakSRTC - Bill Holtzcheiter, Frank Smith III Ames - Glenn Bastiaans, INEEL- Tom Thomas.

Collaboration Type: Mission directed *Collaborator: :* (see description)
Collaborating Organization: (see description)

Description: The objectives of the project are to develop new real-time sensors for characterizing glass melts in high level waste (HLW) and low activity waste (LAW) melters, and to understand the scientific basis and bridge the gap between glass melt model data and melter performance. A basic goal is to characterize glass melts in-situ with the new diagnostic capability so that data will represent the actual melt's behavior. The work will be closely coupled to the needs of the Defense Waste Processing Facility, West Valley Demonstration Project, and vitrification efforts at Hanford, Oak Ridge, and Idaho sites. The project is a collaboration between the MIT Plasma Science and Fusion Center, PNNL, and the Savannah River Technology Center. In addition, discussions are in progress with Tom Thomas of the Tanks Focus Area regarding the possibility of demonstrating with the TFA.

Collaboration Type: Program interaction *Collaborator:* Tom Thomas
Collaborating Organization: Tanks Focus Area

Project: 70052

Title: Material Property Estimation for Direct Detection of DNAPL Using Integrated Ground-Penetrating Radar Velocity, Imaging, and Attribute Analysis
PI: Dr. John Bradford
Institution: University of Wyoming

Multi-offset, ground-penetrating radar data acquisition for DNAPL detection at the SRS. [see Project #70052]

Description: Many DNAPLs, including chlorinated solvents, have much lower dielectric permittivity and conductivity than water. A contrast in electric properties is induced when DNAPL displaces water in the sediment column resulting in an anomalous GPR signature. The focus of our work is direct detection of DNAPLs, specifically chlorinated solvents, via material property estimation from surface ground-penetrating radar (GPR) data. To directly identify zones of DNAPL contamination, we focus on three aspects of reflected wave behavior - propagation velocity, frequency dependent attenuation, and amplitude variation with offset. Velocity analysis provides a direct estimate of dielectric permittivity, attenuation analysis is used to identify variations in conductivity, and AVO behavior is used to estimate the dielectric permittivity ratio at a reflecting boundary. Areas of anomalously low dielectric permittivity and low conductivity are identified as potential DNAPL source zones. We are working with personnel at the Savannah River and Hanford sites to identify contaminated field areas for both controlled experiments and exploratory investigation.

Collaboration Type: Mission directed

Collaborating Organization: Savannah River Technology Center, Hanford Groundwater/ Vadose Zone Integration Project

Project: 70135

Title: Colloid-Facilitated Transport of Radionuclides Through the Vadose Zone

PI: Dr. Markus Flury *Institution:* Washington State University

Description: This project seeks to improve the basic understanding of colloid and colloid-facilitated transport of contaminants in the vadose zone. The objectives are to determine the structure, composition, and surface charge characteristics of colloidal particles formed under conditions similar to those occurring during leakage of waste typical of Hanford tank supernatants, to characterize the mutual interactions between colloids, contaminant, and soil matrix, to evaluate mobility of colloids through soil under different degrees of water saturation and solution chemistry, and to determine the potential of colloids to act as carriers to transport the contaminant through the vadose zone. We are currently in the process of establishing collaboration with other groups working on colloid transport at DOE sites. This interaction includes coordination of research activities and providing colloidal material for testing purposes, and characterization of colloidal materials.

Collaboration Type: Program interaction *Collaborator:* John McCarthy and John Selker

Collaborating Organization: Oak Ridge National Laboratory and Oregon State University

Project: 70165

Title: Integrated Field, Laboratory, and Modeling Studies to Determine the Effects of Linked Microbial and Physical Spatial Heterogeneity on Engineered Vadose Zone Bioremediation

PI: Dr. Fred J. Brockman *Institution:* Pacific Northwest National Laboratory

Description: In situ bioremediation of contaminants can offer advantages in cost, speed, public acceptance, and final cleanup levels achieved relative to physical removal methods. However, the lack of knowledge on how physical and hydrologic features of the vadose zone control the spatial distribution of microbial biotransformation activity and the potential for microorganisms to colonize this region raises questions about the feasibility of deep vadose zone bioremediation, and causes very large uncertainties in the accuracy of current model predictions. Because of the PI's understanding biological processes and bioremediation in the vadose zone, he has been asked by INEEL to write the biological transformation processes portion of the Vadose Zone Complex Wide Science Needs and Capabilities document.

Collaboration Type: Consulting

Collaborating Organization: Idaho National Engineering and Environmental Laboratory

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